

Mpemba effect and phase transitions in the adiabatic cooling of water before freezing

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An accurate experimental investigation on the Mpemba effect (that is, the freezing of initially hot water before cold one) is carried out, showing that in the adiabatic cooling of water a relevant role is played by supercooling as well as by phase transitions taking place at $6 \pm 1^\circ\text{C}$, $3.5 \pm 0.5^\circ\text{C}$ and $1.3 \pm 0.6^\circ\text{C}$, respectively. The last transition, occurring with a non negligible probability of 0.21, has not been detected earlier. Supported by the experimental results achieved, a thorough theoretical analysis of supercooling and such phase transitions, which are interpreted in terms of different ordering of clusters of molecules in water, is given.

A well-known phenomenon such as that of the freezing of water has attracted much interest in recent times due to some counter-intuitive experimental results [1] and the apparent lacking of a generally accepted physical interpretation of them [2], [4], [3], [5]. These results consist in the fact that, *many times*, initially hot water freezes more quickly than initially cold one, a phenomenon which is now referred to as the Mpemba effect (for a short historical and scientific survey see the references in [3]). The observations sound counter-intuitive when adopting the naive, simple view according to which initially hot water has first to cool down to the temperature of the initially cold one, and then closely follow the cooling curve of the last one. The effect takes place even for not pure water, with solutions or different liquids (the original Mpemba observation occurred when he tried to make an ice cream).

Several possible physical phenomena, aimed to explain such observations, have been proposed in the literature, mainly pointing out that some change in water should occur when heated [2] [5].

However, such explanations cannot be applied if some precautions are taken during the experiments (whilst the Mpemba effect has been observed even in these cases) and, in any case, calculations do not seem to support quantitatively the appearance of the effect (see references in [3]).

Some novel light has been introduced in the discussion, in our opinion, in Ref. [3], where the Mpemba effect has been related to the occurrence of supercooling both in preheated and in non-preheated water. Initially hot water seems to supercool to a higher local temperature than cold water, thus spontaneously freezing earlier. As a consequence, such a scenario, apparently supported by experimental investigations, points toward a statistical explanation of the effect, neither the time elapsed nor the effective freezing temperature being predictable.

Here, we prefer to face the problem by starting from

what is known about the *freezing* process, rather than the *cooling* one.

In general it is known that, for given values of the thermodynamic quantities (for example the volume and the energy), a physical system may exist in a state in which it is not homogeneous, but it breaks into two or more homogeneous parts in mutual equilibrium between them. This happens when stability conditions are not fulfilled, so that a phase transition occurs; it is, for example, just the case of water that, at the pressure p of 1 atm and at temperature T of 0°C , becomes unstable.

When liquid water is cooled, the average velocities of its molecules decreases but, even if the temperature goes down to 0°C (the fixed temperature where liquid and solid phases coexist) or lower, this is not a sufficient condition for freezing to start. In fact, in order that ice begins to form, first of all some molecules of the liquid water should arrange in a well-defined order to form a minimum crystal and this, in the liquid state, may happen only randomly. Second, such starting *nucleus* has to attract further molecules in the characteristic locations of the crystalline structure of ice, by means of the interaction forces of the nucleus with the non-ordered molecules in the liquid. Nucleation and crystal growth processes are both favored at temperatures lower than 0°C , so that supercooling of liquid water is generally required before its effective freezing. In fact, in pure water, only molecules in the liquid with statistically lower velocities can arrange the initial nucleus and, furthermore, only slow moving molecules are able to join that cluster and put their kinetic energies into potential energy of bond formation. When ice begins to form, these molecules are removed from those attaining to the given Maxwell distribution for the liquid water, so that the average speed becomes larger, and the temperature of the system rises to 0°C (obviously, the temperature is set at the value where the continuing exchange of molecules is equal in terms of those joining and those leaving the formed crystal surface).

Thus supercooling is, *de facto*, a key ingredient in the freezing process, although supercooled water exists in a state of precarious equilibrium (water is in a metastable

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state). Minor perturbations such as impurities or other can trigger the sudden appearance of the stable crystalline phase for the whole liquid mass, again with the release of the entire crystallization heat (melting heat) which increases the temperature of the freezing liquid to the normal 0°C one.

In general, when a system is in a metastable state, sooner or later it will pass to another stable state. In water, density and entropy fluctuations favor the formation of crystallization nuclei but, if the liquid constitutes a stable state, such nuclei are always unstable and will disappear with time being. However, since the fluctuations become more pronounced the lower the temperature, if water is supercooled, for sufficiently large nuclei they will result to be stable and grew with time, becoming freezing centers. The starting of the phase transition is thus *determined* by the probability of appearance of those nuclei, and the reported Mpemba effect could be simply a manifestation of this process.

We have calculated just this probability P as function of the absolute temperature T of the metastable phase (the one at which the nucleus is in equilibrium with the liquid), obtaining the following result [11]:

$$P = \frac{\alpha}{T_*} \exp \left\{ -\beta \frac{T_*^2}{(T - T_*)^2} \right\}. \quad (1)$$

Here T_* is the equilibrium temperature of the liquid-solid phase, α is a dimensionless normalization factor and β is a constant whose expression is given by

$$\beta = \frac{16\pi\tau^3v^2}{3Q^2kT_*}, \quad (2)$$

where τ is the surface tension, v the molecular volume of the crystallization nucleus, Q the molecular heat of the transition from the metastable phase to the nucleus phase, and k is the Boltzmann constant. Just to give an idea of the macroscopic value of the constant β , let us note that $\tau^3v^2 = W_{\text{surf}}^3$ is the cube of the work done by the surface forces, and by assuming that $Q \sim kT_*$ we may write:

$$\beta \simeq \frac{16\pi}{3} \left(\frac{W_{\text{surf}}}{Q} \right)^3, \quad (3)$$

that is the constant β is ruled by the ratio W_{surf}/Q .

The probability P has a minimum at the liquid-solid equilibrium temperature T_* and increases for decreasing temperature, as expected. From the formulae above it is clear that the probability for nucleation, and thus the onset of the freezing process as well, is enhanced if the work done by the surface forces (or the surface tension itself) is lowered in some way. In normal daily conditions when a commercial refrigerator is employed, this is easily induced in two simple ways: either by the presence of impurities, when solutions (such as an ice cream solution, as in the Mpemba case) are used as the freezing

	$V = 20 \text{ cm}^3$	$V = 50 \text{ cm}^3$	$V = 65 \text{ cm}^3$	$V = 80 \text{ cm}^3$
P_{SC}	1	0.28	0	0.46
	$T_c = -8^\circ\text{C}$	$T_c = -14^\circ\text{C}$	$T_c = -22^\circ\text{C}$	$T_c = -26^\circ\text{C}$
P_{SC}	0.75	0.50	0	0.11

TABLE I: Probabilities for the occurrence of supercooling for different volumes V of the sample and different temperatures of the cryostat T_c .

liquid instead of pure water, or by fluctuations of the external pressure or temperature, caused in the commercial refrigerator itself. This explains why no appreciable supercooling is observed in normal situations. Obviously, the most direct way to induce freezing in supercooled water is to introduce an external body in it, in order to directly lower the surface tension.

We have thus performed an accurate experimental investigation, accounting for a total of about one hundred runs, aimed to clarify the phenomenology of the Mpemba effect and its interpretation. In the first part of our experiments we have tested all the above qualitative predictions about supercooling, by studying the cooling and freezing of tens of cm^3 of normal water in a commercial refrigerator, in daily operation conditions. The key point, in fact, is not to obtain the most favorable physical conditions, employing sophisticated setups, but rather to reproduce the Mpemba conditions, that is adiabatic cooling (with commercial refrigerators) of not extremely small quantities of water. We have used an Onofri refrigerator for the cooling of double distilled water and a NiCr-Ni thermocouple as a temperature sensor (Leybold 666193), interfaced with a Cassy Lab software for data acquisition.

For fixed temperatures of the cryostat we have indeed observed supercooling in our samples, with the freezing occurring just along the lines predicted above. In particular, during the supercooling phase we have induced a number of small perturbations in our samples, namely, variations of external pressure or temperature, mechanical perturbations or introduction of an external macroscopic body (a glass thermometer held at the same temperature of the sample). In *all* these cases we have registered the sudden interruption of the supercooling phase and a practically instantaneous increase of the temperature to the value of 0°C, denoting the starting of the freezing process. Conversely, if no perturbation is induced (or takes places) the water reached an equilibrium with the cryostat at temperatures up to about -30°C (lasting also for several thousands of seconds).

We have then verified that when the freezing process started from the supercooling phase, the Mpemba effect took place with a probability in agreement with that reported in Ref. [3].

In about half (with a total probability of 0.47) of the runs performed we have detected a supercooling phase.

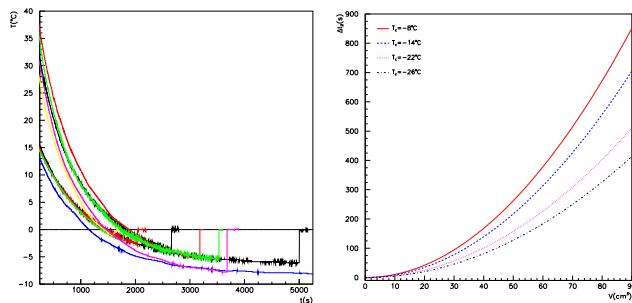


FIG. 1: Left: Cooling curves for $V = 20 \text{ cm}^3$ and $T_c = -8^\circ\text{C}$. Right: The fitted time duration of the phase transition at 3.5°C as function of the volume V of the samples, for different temperatures T_c of the cryostat.

In Table I we report the observed probability P_{SC} for the occurrence of supercooling for different volumes V of the water sample and for different temperatures T_c of the cryostat. We find the data to be fitted by a straight line, denoting (in the range considered) a linear decreasing of P_{SC} for decreasing temperatures of the cryostat and for increasing volumes of the samples, this probability reaching the maximum $P_{SC} = 1$ for $T_c = 0^\circ\text{C}$ (and $V = 0$).

An interesting feature of what we have observed is the sensible appearance of iced water in our samples. In fact, when supercooling did not occur, the ice started to form around the walls of the beaker, while the inner parts were still in a liquid form, as usually expected. Instead the immediate freezing of supercooled water involved the *whole* sample, this showing a very peculiar symmetric form. We have used cylindrical beakers with the temperature sensor in their periphery, near the walls; the observed structure was a pure radial (planar) one, with no liquid water and radial filaments of ice from the center of the beakers to the walls (in one case we have been also able to take a low resolution picture of this, before its destruction outside the refrigerator).

However, although supercooling plays a relevant role in the manifestation of the Mpemba effect, the things are made more complicated by the occurrence of other statistical effects before the temperature of the water reaches the value of 0°C . This comes out when an accurate measurement of the cooling curves is performed (some examples of what we have obtained during the second part of our experiments are reported in Fig. 1).

According to a simple naive model, the heat exchange from the water sample (at initial temperature T_0) to the cryostat (at fixed temperature T_c) is described by the equation

$$C dT = \delta (T_c - T_0) dt, \quad (4)$$

where C and δ are the thermal capacity and the heat conductivity of the water, respectively. Thus by solving the differential equation in (4), the following expression

$T_c = -8 \pm 2^\circ\text{C}$				
	$V = 20 \text{ cm}^3$	$V = 50 \text{ cm}^3$	$V = 65 \text{ cm}^3$	$V = 80 \text{ cm}^3$
Δt_1 (s)	7 ± 1			
Δt_2 (s)	11 ± 6	220 ± 100	500 ± 170	630 ± 160
Δt_3 (s)	12 ± 6		70 ± 30	
$T_c = -14 \pm 2^\circ\text{C}$				
	$V = 20 \text{ cm}^3$	$V = 50 \text{ cm}^3$	$V = 65 \text{ cm}^3$	$V = 80 \text{ cm}^3$
Δt_1 (s)				37 ± 1
Δt_2 (s)	8 ± 3	130 ± 80	480 ± 160	500 ± 60
Δt_3 (s)	7 ± 4			
$T_c = -22 \pm 1^\circ\text{C}$				
	$V = 20 \text{ cm}^3$	$V = 50 \text{ cm}^3$	$V = 65 \text{ cm}^3$	$V = 80 \text{ cm}^3$
Δt_1 (s)		63 ± 1		7 ± 1
Δt_2 (s)		170 ± 100		130 ± 70
Δt_3 (s)				
$T_c = -26 \pm 1^\circ\text{C}$				
	$V = 20 \text{ cm}^3$	$V = 50 \text{ cm}^3$	$V = 65 \text{ cm}^3$	$V = 80 \text{ cm}^3$
Δt_1 (s)		3.5 ± 0.7		
Δt_2 (s)		3 ± 1	320 ± 70	210 ± 170
Δt_3 (s)		200 ± 70	1 ± 1	

TABLE II: Time duration of the phase transitions at 6°C (Δt_1), 3.5°C (Δt_2) and 1.3°C (Δt_3) for different volumes V of the sample and different temperatures of the cryostat T_c .

for the temperature as function of time t is obtained:

$$T = T_c - (T_c - T_0) e^{-t/\tau}, \quad (5)$$

where $\tau = C/\delta$ is a time constant measuring the cooling rate of the sample. However, although the overall dependence of T on time is that expressed by Eq. (5), our experimental data clearly reveal the presence of three transition points before freezing (or supercooling), where τ changes its value. This transitions occur at temperatures $T_1 = 6 \pm 1^\circ\text{C}$, $T_2 = 3.5 \pm 0.5^\circ\text{C}$ and $T_3 = 1.3 \pm 0.6^\circ\text{C}$ with a probability of $P_1 = 0.11$, $P_2 = 0.84$ and $P_3 = 0.21$, respectively. The time duration Δt of each phase transition, during which the temperature keeps practically constant [12], depends on the volume of the sample and on the temperature of the cryostat. The data we have collected are summarized in Table II. For the phase transition at T_2 these data show a linear increase of Δt_2 with T_c and a quadratic one with V ; in Fig. 1 we give the fitting curves corresponding to best fit function $\Delta t_2 = (a + bT_c)V^2$. Instead, for the other two phase transitions no sufficient data are available in order to draw any definite conclusion on the dependence on V and T_c , though Δt_1 and Δt_3 appear to be shorter than Δt_2 .

The occurrence of these phase transitions is likely related to the formation of more or less ordered structures in water, resulting from the competition between long-range density ordering and local bond ordering maximizing the number of local bonds [8]. The anomalous density maximum at about 4°C (which we observe here at $T_2 = 3.5 \pm 0.5^\circ\text{C}$) is, for example, explained just in

	$T_c = -8^\circ\text{C}$	$T_c = -14^\circ\text{C}$	$T_c = -22^\circ\text{C}$	$T_c = -26^\circ\text{C}$
τ_1 (s)	600 ± 110	680 ± 100	1000 ± 110	950 ± 190
τ_2 (s)	1080 ± 260	1060 ± 170	530 ± 90	570 ± 3
τ_3 (s)	1590 ± 930	1520 ± 730	270 ± 50	220 ± 80
τ_4 (s)	620 ± 480	500 ± 180	150 ± 30	640 ± 490

TABLE III: Time constants τ_1 ($T < T_1$), τ_2 ($T_1 < T < T_2$), τ_3 ($T_2 < T < T_3$), τ_4 ($T > T_3$) of the cooling curves before and after the three phase transitions detected, for different temperatures of the cryostat T_c .

term of this: as water is cooled, the local specific volume increases due to the progressive increase in tetrahedral order, so that the entropy, that always decreases upon cooling, at 4°C becomes anticorrelated with the volume, resulting in an inversion (from positive to negative) of the thermal expansion coefficient and a corresponding density maximum [9]. Similar explanations in terms of different ordering could apply also to the other two transitions we have observed, but an exhaustive discussion of them, which would require more experimental data, is beyond the scope of this Letter. We only note that, while the first transition at $T_1 = 6 \pm 1^\circ\text{C}$ seems related to the effect observed in Ref. [10] at 8°C , to the best of our knowledge no other author has reported the one at $T_3 = 1.3 \pm 0.6^\circ\text{C}$ (which, as mentioned, occurs with an appreciable probability of 0.21).

The observed mean values of the four time constants of the cooling curves, before and after the three phase transitions, are reported in Table III for different values of T_c . All the time constants are approximately *independent* on the volume V , in disagreement with the naive model discussed above which predicts an increase of τ with the thermal capacity. Instead they depend linearly on T_c , showing a negative slope for τ_1 and positive ones for τ_2, τ_3, τ_4 and a finite value for $T_c = 0^\circ\text{C}$. Note that (in the naive model) the ratios of the different time constants, at fixed volumes, give the (inverse) ratios of the heat conductivities in the different ordered phases (all these ratios decrease with the cryostat temperature), which are directly related to microscopic quantities like the size and average velocity of the ordered clusters of molecules in water.

Coming back to the Mpemba effect, it is easy to see that Eq. (5) predicts that, for constant τ , initially hot water reaches the freezing point *later* than initially cold water. However, from what just discussed, in general this could be no longer true if the time constant changes its value during the cooling process (the slope of the cooling curves changes), or phase transitions before freezing occur (with time durations sufficiently long/short). In addition to these effects, the reaching of the freezing point does not automatically guarantees the effective starting of the freezing process, since relevant supercooling may take place, thus statistically causing the freezing of ini-

tially hot water *before* cold one.

From the data we have collected we have verified that, for given V and T_c , in many cases no inversion between the cooling curves happens before the freezing point, irrespective of the change in the value of τ or the time duration of the phase transitions. Nevertheless we have as well realized that this is mainly due to the not very large difference between the initial temperatures of the samples, and in few cases (among those studied by ourselves) it cannot be applied, the largest effect causing the inversion being the phase transition at T_2 .

In conclusion our experimental results, and their interpretation reported here, clearly point out the statistical nature of the Mpemba effect (as already realized in [3]), whose explanation is given in terms of transitions between differently ordered phases in water and supercooling. The very detection of such phenomena seems to require the cooling to be adiabatic (as fulfilled in our experiment, as well as in those performed by other authors [3]), since for non adiabatic processes (for example, in fused salt) the coexistence of local solid nuclei in the liquid phase has been observed [13].

An unexpected novel transition at $T_3 = 1.3 \pm 0.6^\circ\text{C}$ has been as well detected with a non negligible probability, calling for further accurate investigation in order to achieve a more complete understanding of the unique properties of water.

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 - [11] We do not give the details of such calculations; the interested reader may follow those reported in section 162 of Ref. [7] for a similar case.
 - [12] In some cases we have been able to observe also a van der Waals-like profile of $T(t)$ at the transition point (metastable state), instead of only the mean constant value of T .
 - [13] We are indebted with M. Villa for having pointed out this to us.